

Structure and Stability of an Amorphous Metal

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Using molecular dynamics simulations, with a realistic many-body embedded-atom potential, and a novel method to characterize local order, we study the structure of pure nickel during the rapid quench of the liquid and in the resulting glass. In contrast with previous simulations with pair potentials, we find more crystalline order and fewer icosahedra for slower quenching rates, resulting in a glass less stable against crystallization. It is shown that there is not a specific amorphous structure, only the arrest of the transition from liquid to crystal, resulting in small crystalline clusters immersed in an amorphous matrix with the same structure of the liquid.

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The detailed knowledge of the atomic structure is essential to understand the special properties of amorphous materials. There seems to be general agreement in that the basic process underlying the glass transition is the arrest of structural relaxations [1], but it is not clear to what extent this leads to new structural units. Very different structural models have been proposed [2], and some of them assume that the glass structure is essentially different from those of the liquid and the crystal. For close-packed systems, the icosahedron has been largely proposed as a characteristic configuration, which becomes predominant during liquid quenching. Another example is the polycluster model [3], in which the amorphization proceeds by the nucleation and growth of amorphous clusters within the liquid.

However, like in liquids and defective solids, the lack of atomic periodicity makes the experimental determination of the structure a largely unsolved problem. Therefore, molecular dynamics simulations offer an invaluable complementary tool, although the simulated times are generally much shorter than the experimental quenches. A common strategy is to study model systems with simple interactions, hoping that they will describe qualitatively the properties of real glasses. Thus, systems simulated with pair potentials show an increase of icosahedra during liquid cooling [4–7]. However, the structural properties depend strongly on the type of interatomic potential used [8], and some simulations indicate that the formation of icosahedra decreases when many-body effects or nonadditivity are included [9]. Therefore, it is questionable to what extent these results can be extrapolated to real glasses.

An alternate strategy is to focus on systems, like pure metals, whose natural relaxation times are so short that they can be actually simulated in the limit between glass formation and crystallization. Within this approach we show in this work that, in the case of a pure metal, there is no specific amorphous structure different from that of the liquid and the crystal, but only the arrest of the transition from one to the other. We also study the stability of the glass and, in contrast with recent works [4,10], show that it is more stable when quenched faster.

Although the experimental quenching rates required to form their glasses are extremely fast, the possible applications of pure amorphous metals make their study a field of much current interest [11,12]. In this work we have simulated the formation of pure amorphous nickel using a realistic embedded-atom potential [13]. It belongs to a broad class of potentials [13,14] with the general functional form:

$$U = \sum_{i < j} V(r_{ij}) + \sum_i F \left(\sum_{j \neq i} \rho(r_{ij}) \right) \quad (1)$$

The first term typically represents the repulsion of overlapping ionic cores. The second term is the energy of immersing an atom in the electron density produced by its neighbors, and represents the metallic bond. This type of potential has proven to reproduce very well the basic structural and dynamical properties of solids, surfaces, defects, liquids [15] and glasses [16] of transition and noble metals. Thus, although our calculations were performed for the specific case of nickel, we expect that the qualitative conclusions will remain valid for a wide set of pure metals. To make the simulation more realistic, we use constant temperature and pressure molecular dynamics, thus allowing energy and volume fluctuations which may be critical to the resulting dynamics close to the glass transition. In particular, it is well known that the glass formation tendency of many materials depends strongly on the pressure [17].

The simulated system consists of 6912 atoms in a cubic cell with periodic boundary conditions, initially equilibrated at 2000 K, well above the melting temperature. The Newton equations were integrated using the Verlet algorithm with a time step of 5 fs. The temperature and pressure were fixed by rescaling the atomic velocities and positions at every time step. The pressure was kept always zero, while the temperature was reduced linearly from 2000 K to 100 K at different cooling rates, from 8×10^{12} to 10^{14} K/s. The systems were finally equilibrated at 100 K during 160 ps to prove their stability. Following Stillinger [18], to analyze the structure at arbitrary temperatures without

the vibrational noise, we always relax first the system to its closest local minimum by a conjugate gradient energy minimization. To characterize the atomic environments, we have generalized the method of Steinhardt *et al.* [7], based on the rotationally invariant moments:

$$Q_l = \frac{1}{N_n} \left(\sum_{ij}^{N_n} P_l(\cos \theta_{ij}) \right)^{1/2} \quad (2)$$

where N_n is the number of nearest neighbors of the atom (closer than the first minimum in the radial distribution function), θ_{ij} are the angles formed by two neighbors (with the reference atom in the vertex), and P_l are Legendre polynomials. The Q_l 's, with $0 \leq l \leq 10$, may be considered as the components of a vector. If the euclidean distance from this vector to that of the fcc, hcp or icosahedral environments is less than certain tolerances, the atom has that environment distorted in some degree [19]. Varying these tolerances in a wide range did not change qualitatively any of the results reported. For the embedded atom potential used, the fcc and hcp structures are essentially degenerate and they are present in almost equal proportions. On the contrary, the number of atoms with bcc environment is negligible. Therefore, we have analyzed the results in terms of crystalline (fcc+hcp) and icosahedral structures only. In addition, as clusters of four-atom tetrahedra (i.e. regular face-sharing tetrahedra) have been also proposed as the basic building blocks in amorphous metals, we also analyze them. We define a regular tetrahedron as four neighbor atoms whose relative distances differ by less than 0.55 % [20].

During the simulated quench, the heat capacity C_P presents a clear discontinuity at $T_g \sim 750$ K, which agrees well with the experimental glass transition temperature estimated for pure nickel [21]. Although the drop in C_P is rather smooth because of the fast quenching rates, it is generally accepted that this discontinuity is associated with the arrest of structural relaxation, which prevents the system from visiting all the possible configurational states and is the landmark of the glass transition. Thus, it can be said that pure nickel exhibits a glass transition. As expected, T_g increases moderately with the quenching rate. It is important to stress that a slower quench at 7×10^{12} K/s resulted in a complete crystallization. Therefore, we are studying the slowest rates which result in an amorphous state. Fig. 1 compares the radial and angular distribution functions of the liquid with those of one of the amorphous structures (excluding as central atoms those with crystalline environment). It is clear that they are almost identical. The double second peak in $g(r)$, characteristic of amorphous metals, is clearly visible but, contrarily to previous proposals [22], it is not related with icosahedra (which are very scarce, see below). In fact, it is not even characteristic of the amorphous state, since it also appears in liquid configurations (relaxed to the closest local minimum).

Fig. 2 shows the final number of atoms with crystalline and icosahedral environments for all the quenches. Two features are worth noting. First, the final number of crystalline atoms is proportional to the total quench time. This means that the rate of growth of crystalline order during the quench is approximately independent of the quenching rate. Second, the number of atoms with icosahedral environment is small at all temperatures and it even decreases during the slowest quenches. The size of the tetrahedra clusters (not shown) also decreases. This is in marked contrast with pair-potential simulations, in which icosahedra and tetrahedra clusters grow at the quench and only disappear during crystallization [4,10,20]. Typically, free (gas phase) icosahedral clusters are more stable than pieces of fcc or hcp structures, due to the higher coordination on their surface, so that a crystalline cluster needs to grow beyond some critical size to become energetically favorable [23]. This is still true with the embedded-atom potential for free nickel clusters, but not for clusters immersed in a liquid or amorphous matrix, which have ~ 30 meV/atom more energy than crystalline clusters. On the contrary, in pair potential models, atoms with icosahedral environment have the lowest energy [4,22], so that more abundant [5] and more stable [4] icosahedra are formed with slower quenches.

To address the question of how much aggregation exists among the atoms with crystalline environment, Fig. 3 shows the three-dimensional structure of some of the 6912-atom samples produced at different quenches. Only atoms with crystalline environment are shown, and clusters of them are clearly visible. These clusters, if not perfectly crystalline, are regions with good local order. Larger crystalline clusters are observed for the slowest quenches. In agreement with our results, it has been observed very recently that amorphous nickel consists of regions with only short range order, together with regions of nascent crystallinity [24].

In order to study the relative stability of the glasses produced at different quenching rates, we heated slowly three samples, now with 856 atoms because the slow heating rates require more computational effort. These samples had been quenched at different cooling rates and had correspondingly different proportions of crystalline atoms. The same heating rate of 3×10^{12} K/s was used for all three samples. Fig. 4 illustrates such reheating, showing a sudden drop in energy when the samples crystallize. It is clear that the more slowly cooled (and more crystalline) samples are less stable, crystallizing at a lower temperature. We repeated the same procedure for three more samples, with the same result. A visual inspection shows that crystallization occurs by the growth of crystallites initially present. Our results are again in contrast with those for pair potentials [4,10], but they are in agreement with the experimental observation that the most slowly cooled side of a metallic glass ribbon crystallizes first [25]. In fact, crystallization

in metallic glasses happens frequently by the growth of quenched-in nuclei, which are more numerous after slower quenches [26].

From the above results and from the slower simulated quenches, which resulted in complete crystallization, the picture which emerges for the formation and the structure of pure amorphous metals is particularly simple. As the liquid is cooled down, the rate of nucleation and growth of crystallites reaches a maximum, determined by the increasing difference in free energies and the decreasing rate of the dynamics. This maximum approximately coincides with the glass transition, because the arrest of the dynamics is also the origin of the latter. The slower the quenching rate, the larger the crystallites, which grow immersed in an amorphous matrix with essentially the same structure of the liquid. The crystallites are well separated from each other until the proportion of crystalline atoms is $\sim 30\%$. If this limit is not reached, no clear signs of crystallization appear, neither in the heat capacity nor in the resulting pair correlation function. Above this limit, the crystallization proceeds by the growth of the preexisting crystallites, accelerating because of their mutual interaction [27,28], and producing a clear energy discontinuity. The resulting structure is then an aggregate of space-filling and well formed crystallites, with a very different pair correlation function.

In conclusion, we have found that in pure amorphous metals there are no special structural motifs, as in the icosahedral or polycluster models [2,3]. Instead, there is a continuous change from liquid to crystal, arrested by the fast quench. But, despite the absence of a special structure, this system shows the most characteristic properties of the glass transition, and of the amorphous solid state. In this sense, pure metals are the simplest glasses, showing only their essential kinetic and thermodynamic properties (deriving from the arrest of the relaxation dynamics), but devoid of complex structural changes. As such simplest systems, pure metals might help to clarify many of the subtle properties of glasses.

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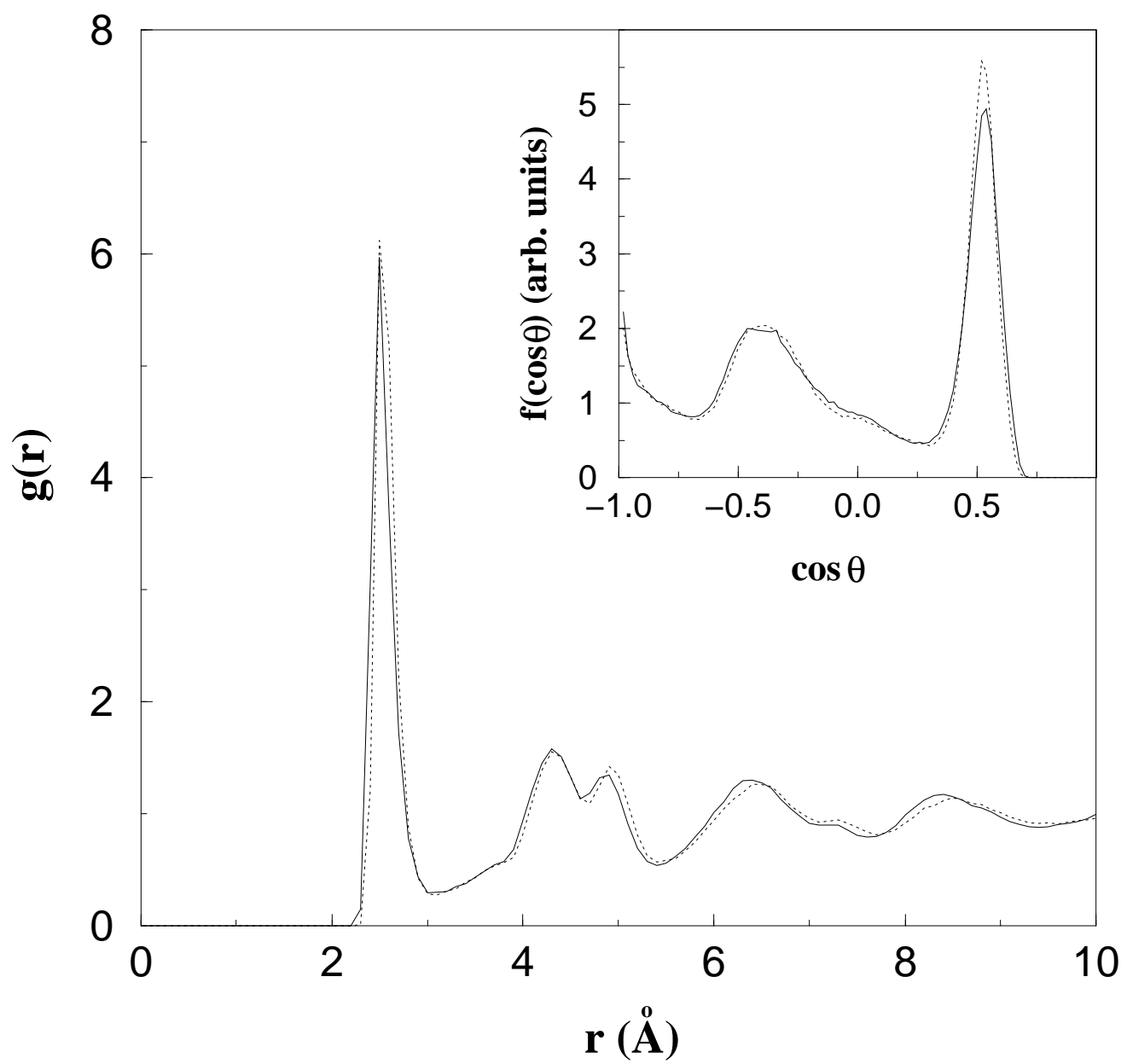
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- [28] In this case the final number of crystalline atoms deviates above the straight line of figure 2.

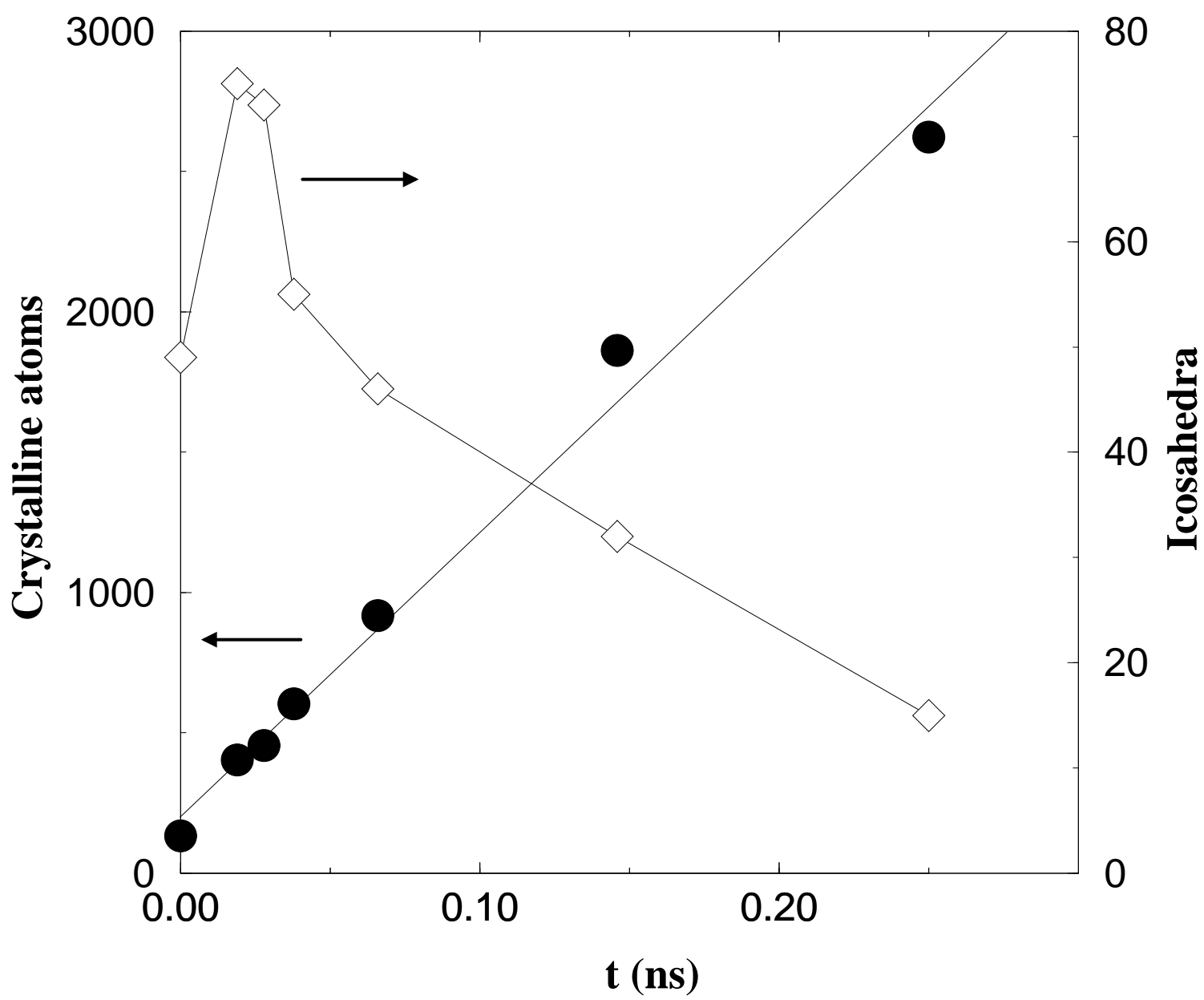
FIG. 1. Radial (main figure) and angular (inset) distribution functions of the liquid (dashed) and of one of the amorphous samples, quenched at 3×10^{13} K/s (solid). In the latter, to show the structure of the pure amorphous matrix, only the distribution functions of the amorphous atoms (with non-crystalline environment, see text) with all their neighbours are represented. In both cases, the structure was first relaxed to the closest energy minimum in order to avoid the vibrational noise. The slight shift between both curves in $g(r)$ is mainly due to thermal expansion.

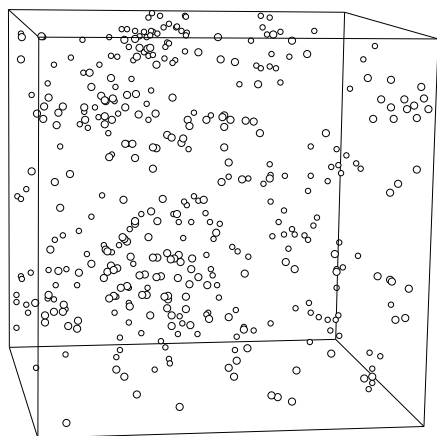
FIG. 2. Number of atoms with crystalline (circles) and icosahedral (diamonds) environment in the amorphous samples with 6912 atoms, quenched from the liquid at different rates. t is the total time spent for the quench, from 2000 K to 100 K. The liquid configuration is represented at $t = 0$. The lines are a linear fit and a guide to the eye. Notice the different scales.

FIG. 3. Simulation cells with the final configuration of samples quenched at different rates. Only atoms with crystalline environments are shown. Quenching rates decrease from a to d . a : 10^{14} K/s, b : 5×10^{13} K/s, c : 3×10^{13} K/s, d : 10^{13} K/s.

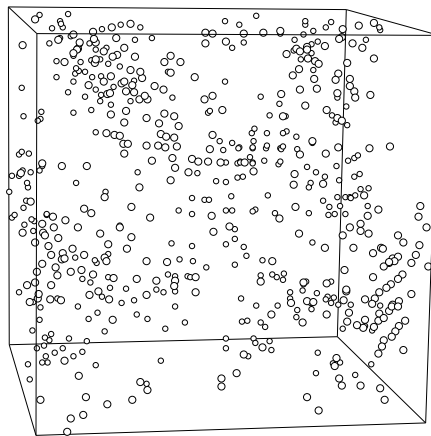
FIG. 4. Heating and crystallization of three amorphous samples, previously quenched at different rates. The numbers indicate the amount of crystalline atoms existing in the relaxed samples before heating.



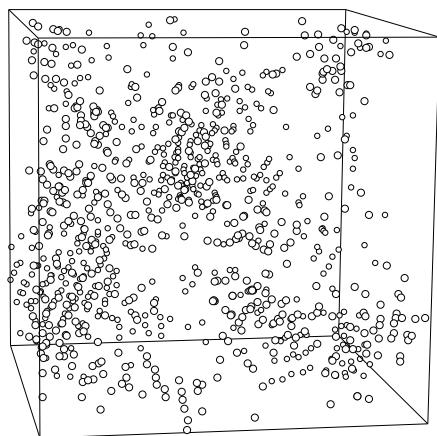




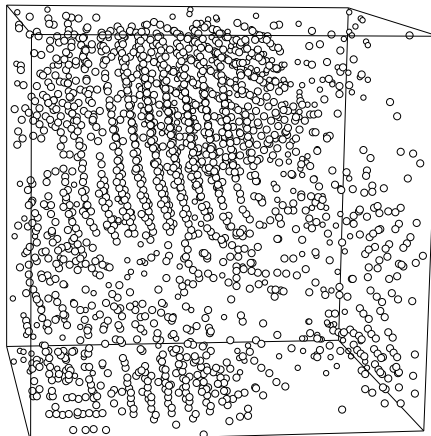
a



b



c



d

